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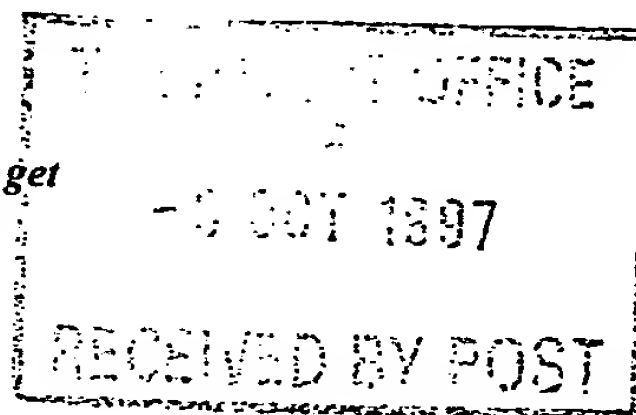
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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

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4. Title of the invention

Bistable Nematic Liquid Crystal Device

5. Name of your agent *(if you have one)*

J B Edwards

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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PATENT APPLICATION

BISTABLE NEMATIC LIQUID CRYSTAL DEVICE

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File Ref: DERA/HO/COM/IPD01/P2619

15   Filed: 1997

Note: this invention was made under an arrangement with HP

Slippery Surfaces cases:

20   1   (P2618) general case genslip.1 - cover all the following file on same day

2   **(P2619) bistable case - bislip1.doc   was pat4 etc involves HP**

3.   (P2620) twisted nematic tnslip1.doc improves TN devices was pat5 etc

4   (P2621) ferro electric   - feslip1.doc   improves FELCDs

25

BISTABLE NEMATIC LIQUID CRYSTAL DEVICE

This invention relates to bistable nematic liquid crystal devices.

Liquid crystal devices typically comprise a thin layer of a liquid crystal material contained between cell walls. Optically transparent electrode structures on the walls allow an electric field to be applied across the layer causing a re-ordering of the liquid crystal molecules.

There are three known types of liquid crystal material, nematic, cholesteric, and smectic each having a different molecular ordering. The present invention concerns devices using nematic materials.

In order to provide displays with a large number of addressable elements it is common to make the electrodes as a series of row electrode on one wall and a series of column electrodes on the other cell wall. These form e.g. an x, y matrix of addressable elements or pixels and, for twisted nematic types of devices, are commonly addressed using rms. addressing methods.

Twisted nematic and phase change type of liquid crystal devices are switched to an ON state by application of a suitable voltage, and allowed to switch to an OFF state when the applied voltage falls below a lower voltage level. i.e. these devices are monostable. An advantage of nematic type of devices is the relatively low voltage requirements. They are also mechanically stable and have wide temperature operating ranges. This allows construction of small and portable battery powered displays. A disadvantage of such devices is their monostable switching characteristic which limits the number of lines that can be multiplex addressed.

Another way of addressing large displays is to use a bistable liquid crystal device. Ferroelectric liquid crystal displays can be made into bistable device with the use of smectic liquid crystal materials and suitable cell wall surface alignment treatment.

5 Such a device is a surface stabilised ferroelectric liquid crystal device (SSFELCDs) as described by:- L J Yu, H Lee, C S Bak and M M Labes, Phys Rev Lett 36, 7, 388 (1976); R B Meyer, Mol Cryst Liq Cryst, 40, 33 (1977); N A Clark and S T Lagerwall, Appl Phys Lett, 36, 11, 899 (1980). One disadvantage of ferroelectric devices is the relatively large voltage needed to switch the material. This high voltage

10 makes small portable, battery powered displays expensive. Also these displays suffer from other problems such as lack of shock resistance, limited temperature range and also electrically induced defects such as needles.

If a bistable switching characteristic can be achieved using nematics then a display can

15 be made which has the merits of both the above mentioned technologies but without their problems.

It has already been shown by Durand et al that a nematic can be switched between two alignment states via the use of chiral ions or flexoelectric coupling: A Charbi, R

20 Barberi, G Durand and P Martinot-Largarde, Patent Application No WO 91/11747, (1991) "Bistable electrochirally controlled liquid crystal optical device", G Durand, R Barberi, M Giocondo, P Martinot-Largarde, Patent Application No WO 92/00546 (1991) "Nematic liquid crystal display with surface bistability controlled by a flexoelectric effect".

25

Patent US 4,333,708 describes a multistable liquid crystal device in which cell walls are profiled to provide an array of singular points. Such substrate configurations provide multistable configurations of the director alignments because disclination must be moved to switch between stable configurations. Switching is achieved by

30 application of electric fields.

Patent Application No:. WO97/14990. (PCT-96/02463. GB95 21106.6) describes a bistable nematic device having a grating surface treatment to at least one cell wall that permits nematic liquid crystal molecules to adopt either of two pretilt angles in the

5   same azimuthal plane. The cell can be electrically switched between these two states to allow information display which can persist after the removal of power.

Another bistable nematic device is described in GB.2,286,467-A. This uses accurately formed bigratings on at least one cell wall. The bigrating permits liquid crystal

10   molecules to adopt two different angular aligned directions when suitable electrical signals are applied to cell electrodes. e.g. dc coupling to flexoelectric polarisation as described in Patent Application No. WO.92/00546. Since in the two splayed states the director is quite close to being in the plane of the layer. the coupling between director and flexoelectric component can be small. which may hinder switching in some

15   circumstances.

The bistable nematic device of GB2286467-A also has a further problem which is not present in ferroelectric devices, that is. the need to switch the surface layer of molecules in order to eliminate image sticking effects. Surface layer switching usually

20   requires high voltages which leads to both high power consumption and the need for customised driver circuitry.

According to this invention the problem of surface layer switching is reduced by using a surface treatment which changes the liquid crystal properties in the vicinity of the surface and so leads to a lower anchoring energy between the liquid crystal and the

5   surface. This allows lower voltage operation without compromising other device parameters. .

According to this invention a bistable nematic liquid crystal device comprises:

10   two cell walls enclosing a layer of nematic liquid crystal material:

electrode structures on both walls:

a surface alignment on both cell walls providing alignment direction to liquid crystal

15   molecules:

means for distinguishing between switched states of the liquid crystal material:

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20

means for reducing inelastic azimuthal memory anchoring energy in the surface alignment on one or both cell walls.

Ideally the inelastic azimuthal memory anchoring energy is reduced to zero.
Preferably the zenithal anchoring energy is also reduced.

5   The means for reducing energy may be an oligomer or short chain polymer which is
either spread on the surface or added to the liquid crystal material.

Preferably the oligomer or short chain polymer does not change the pretilt by a
substantial amount. e.g. change the pretilt by more than 5°.

10

The treatment is used in conjunction with a surface which induces bistable nematic
alignment

The bistable surface may be a surface alignment bigrating on at least one of the cell
15   walls that permits the liquid crystal molecules to adopt two different azimuthal
alignment directions, as in patent application WO97/14990, (PCT-96/02463. GB95
21106.6).

The angle between the alignment directions may 90° or less than 90°.

20

The grating may be a profiled layer of a photopolymer formed by a photolithographic
process e.g. M C Hutley. Diffraction Gratings (Academic Press. London 1982) p 95-
125; and F Horn. Physics World, 33 (March 1993). Alternatively, the bigrating may
be formed by embossing: M T Gale, J Kane and K Knop. J App. Photo Eng. 4. 2. 41
25   (1978), or ruling; E G Loewen and R S Wiley. Proc SPIE. 88 (1987), or by transfer
from a carrier layer.

The bigrating may have a symmetric or asymmetric groove profile. In the latter case the surface induces both alignment and pretilt as described in GB2286467-A.

5   The gratings may be applied to both cell walls and may be the same or different shape on each wall.

The bistable surface could alternatively be formed by using an obliquely evaporated material as described in patent Application WO 92/0054 (G Durand. R Barberi. M. 10   Giocondo and P Martinot-Largarde. 1991).

The cell walls may be substantially rigid e.g. glass material, or flexible e.g. polyolefin.

The electrodes may be formed as a series of row and column electrodes arranged and 15   an x,y matrix of addressable elements or display pixels. Typically the electrodes are 200μm wide spaced 20μm apart.

Alternatively, the electrodes may be arranged in other display formats e.g. r-θ matrix or 7 or 8 bar displays.

The invention will now be described. by way of example only with reference to the accompanying drawings of which:

5   Figure 1 is a plan view of a matrix multiplexed addressed liquid crystal display;

Figure 2 is the cross section of the display of figure 1;

Figure 3 shows the threshold voltage for random bistable switching as a function of
10   pulse length for two cells, one with a weak anchoring treatment and one with conventional strong anchoring.

Figure 4 shows the configuration for off-axis photolithography used in the fabrication of grating structures with asymmetric groove profiles.

15

The display in figures 1, 2 comprises a liquid crystal cell 1 formed by a layer 2 of nematic or long pitch cholesteric liquid crystal material contained between glass walls 3, 4. A spacer ring 5 maintains the walls typically 1-6μm apart. Additionally numerous beads of the same dimensions may be dispersed within the liquid crystal to maintain
20   an accurate wall spacing. Strip like row electrodes 6 e.g. of SnO_2 or ITO are formed on one wall 3 and similar column electrodes 7 are formed on the other wall 4. With m-row and n-column electrodes this forms an m×n matrix of addressable elements or pixels. Each pixel is formed by the intersection of a row and column electrode.

A row driver 8 supplies voltage to each row electrode 6. Similarly a column driver 9 supplies voltages to each column electrode 7. Control of applied voltages is from a control logic 10 which receives power from a voltage source 11 and timing from a

5 clock 12.

Either side of the cell 1 are polarisers 13. 13' arranged with their polarisation axis substantially crossed with respect to one another. The input polariser is parallel to one alignment state for the case where the alignment states differ in azimuthal angle by 90°

10 . An additional optical compensator such as a stretched plastic film may also be added between the liquid crystal cell and one of the polarisers.

A partly reflecting mirror 16 may be arranged behind the cell 1 together with a light source 15. These allow the display to be seen in reflection and lit from behind in dull

15 ambient lighting. For a transmission device. the mirror may be omitted.

Prior to assembly, at least one of the cell walls 3. 4 are treated with alignment gratings to provide a bistable alignment. i.e. two stable alignment directions shown as R.R' 45° apart. but may be 90°. For example the alignment may be provided by a bigrating

20 with symmetric and asymmetric profiles to give both alignment and a required amount of pretilt. Techniques for producing bigratings to give bistable nematic devices are described in GB-A-2.286,467 (PCT-WO-95/22077) and WO97/14990. (PCT-96/02463, GB95 21106.6).

25 The second surface of the cell (if not provided with a bigrating) may be treated with either a planar or homeotropic monostable surface.

Conventional alignment techniques provide pretilt (zenithal) and alignment direction (azimuthal) with substantial anchoring energy. This means that switching of the device under the influence of electric fields results in movement of the liquid crystal

5   molecules mostly in the centre of the layer, and zero movement at and adjacent the wall surface. Both pretilt and alignment direction are necessary for good device performance. What is wanted is pretilt values and alignment together with reduced anchoring energy so that molecules at or adjacent the cell walls can move under the application of normal voltage levels.

10

The present invention provides such a wanted pretilt and alignment together with lowered surface anchoring energy. The invention does this, in one example, by inclusion of oligomer units in the liquid crystal layer 2 and which preferentially migrate to the cell wall surfaces.

15

An explanation of anchoring energy is as follows:

In general anchoring of a nematic liquid crystal on a surface can be described by three macroscopic parameters, pretilt, zenithal anchoring energy and azimuthal anchoring

20   energy.

Consider a surface in the x-y plane (parallel to a cell wall). The pretilt (θ_p) is defined as the preferred angle of inclination of the nematic director with respect to the x-y plane. To change the tilt of the surface director from θ_p to an arbitrary tilt θ, an energy per unit area of W must be supplied to the system where [A. Rapini and M. Papoular. J. Phys. (Paris), 36, C-1, 194 (1975)]:

$$W = W_\theta \sin^2(\theta - \theta_p) \tag{1}$$

W_θ is the zenithal anchoring energy and represents the energy required in order change the tilt of the surface director by 90°. If the director has a preferred in-plane orientation, say along the x axis, then an energy must be supplied to the system to change this orientation. The energy is now given by

$$W = W_\phi \sin^2 \phi \tag{2}$$

where ϕ is the change in the in-plane orientation and W_ϕ is the azimuthal anchoring energy.

Pretilt and zenithal anchoring can be achieved from most solid surfaces while azimuthal anchoring usually requires some extra treatment in order to obtain a preferred in-plane direction such as an anisotropic polymer or a surface grating.

For most surfaces W_θ and W_ϕ are large and so reorientation of the director at the surface only occurs at high voltages. Bistable nematic switching relies on surface director reorientation and in order to achieve low voltage switching the above quantities must be reduced.

Furthermore any additional inelastic memory azimuthal anchoring (P. Vetter et al. Euro Display 1993. SID. p.9) due to microscopic absorption of the first nematic layer into the surface must be removed. This anchoring memory may have the effect of

5 pining molecules in a given position (e.g. between the two switched states) to which they may return after removal of a voltage. Ideally this memory should be completely removed so that the molecules remain in their switched positions after removal of voltages. In practice, reduction rather than complete removal can be satisfactory.

10 Three examples of the weak anchoring treatment applied to a bistable surface are now given:

Example 1

15 The treatment consists of adding a small (1-10%) amount of a UV curing adhesive material to the nematic prior to cell filling. Examples of suitable materials include N65, N63, N60 or N123 (All manufactured by Norland Products Incorporated. North Brunswick, NJ, USA). In this particular example. one of these materials (N65) is used.

20 In the first experiment this material was added to nematic E7 in concentrations of 1%, 2%, 4% and 6%. The mixture was then used to fill cells whose inside walls were coated with flat polymer layers, without any alignment direction. The purpose of this experiment was to confirm a weakening of the surface anchoring with the addition of N65. Surfaces were prepared using a layer of photoresist (Shipley 1805) which was

25 hardbaked to 160°C to ensure insolubility in the liquid crystal.

Cells were made using these surface with a gap of 10μm. Each was filled with a different concentration of N65 including a control sample of pure E7. Filling was carried out in the isotropic phase (65°C) followed by slow cooling to room

5 temperature, and without exposure to UV light. All cells showed a random planar alignment of the nematic which is also called a Schlerien texture. In the case of the pure E7, 1% N65 and 2% N65, the texture could not be moved by applying finger pressure to the cell walls whereas for the 4% and 6% mixtures, the texture was highly mobile and domain walls could be easily moved by applying small amounts of

10 pressure. Once the domain walls had been moved they did not return to their original position but instead remained in the new position for longer than several days. Therefore the 4% and 6% mixtures lead to a loss of memory anchoring.

A second similar experiment was carried out in which the cells were exposed to UV

15 radiation after filling but before cooling to room temperature. In this case the 4%, 6% and also the 2% mixtures showed room temperature domain wall mobility. The improvement in the 2% mixture can be explained as follows. The N65 material contains both esters and acrylate monomers which polymerise under UV radiation to form oligomer units which then join together to form larger polymer chains. If the 2%

20 solution is cured for a short time then the reaction can be terminated when only oligomer units have been formed. The oligomers do not phase separate from the liquid crystal but they so migrate preferentially to the surface in order to minimise the surface free energy. This has the effect of diluting the amount of liquid crystal at the surface which leads to an effective reduction in the order parameter, S which is defined by (P.

25 G. deGennes, The Physics of Liquid Crystals, Clarandon Press, Oxford 1974):

$$S = \frac{1}{2}\left\langle\left(3\cos^2\theta - 1\right)\right\rangle \qquad (3)$$

The reduction in nematic order due to a oligomer concentration has the twofold effect of screening the liquid crystal from the surface which removes the memory anchoring as well as reducing the elastic anchoring energy, W_θ. The uncured material also has this effect but must be added in a greater concentration (>4%) as the acrylate monomer does not preferentially migrate towards the surface.

The cured material containing 2% N65 was then removed from the cell in which it was cured and used to fill another cell. This second cell also showed a highly mobile Schlerien texture demonstrating that the weak anchoring effect is due to the additive in the bulk as opposed to any surface layer formed during curing.

The next set of experiments were designed to show the effect of the N65 treatment on the zenithal anchoring energy, W_θ. This quantity can be calculated by measuring the saturation voltage, V_s. That is, the voltage at which the director tilt in the cell is perpendicular to the surface throughout the thickness of the cell. In practice this is measured by observing when the transmitted intensity of the Schlerien texture falls to zero when viewed between crossed polarisers. W_θ is then given by

$$W_\theta \approx \frac{3.85\sqrt{\varepsilon_o \Delta\varepsilon \, k_{11}} \cdot V_s}{d} \tag{4}$$

where d is the liquid crystal layer thickness. k_{11} is the liquid crystal splay elastic constant and $\Delta\varepsilon$ is the liquid crystal permittivity anisotropy.

Results are shown in Table 1. The pure E7 cell failed to show a black state before cell breakdown and so only a lower limit on W_θ can be given. In the cases of the E7 containing N65, the curing was performed in a fused silica cell prior to transferring the mixture to a separate measurement cell. The exposure was carried out using an unfiltered mercury lamp with an optical output of $2.0mW/cm^2$.

Cell mixture	Cure time (m)	W_θ (N m^{-1})
Pure E7	-	$>5\times10^{-2}$
2% N65 in E7	5	5.4×10^{-3}
2% N65 in E7	10	6.3×10^{-3}
2% N65 in E7	30	7.7×10^{-3}
2% N65 in E7+ pure E7 (1:1)	10	8.0×10^{-3}

Table 1

Surface zenithal anchoring energies modified by the presence of N65.

Greater cure times are found to lead to stronger anchoring which is consistent with the formation of longer polymer chains which tend to phase separate from the nematic rather than lower its surface order parameter. One set of data shows that the anchoring energy can also be adjusted by diluting the N65/E7 mixture in pure E7. In all cases the percentage of N65 during the cure process was kept to 2% to ensure consistent reaction kinetics.

The above results confirm that the N65 treatment leads to a loss of in-plane memory anchoring as well as lowering (by about an order of magnitude) the zenithal anchoring energy. The next stage is to test the effect of the treatment on the switching of a bistable nematic device.

One example of a surface which can offer bistable nematic alignment is a surface bigrating (as described in GB2286467-A.) prepared in a manner similar to that shown in Figure 4. In this case samples were made by spin coating 1805 photoresist 20 onto

5 ITO coated glass 21 at a spin speed of 3000 rpm to give a coating thickness of 0.55μm. The samples were then softbaked at 90°C for 30 minutes. The bigrating was exposed through a mask 22 using hard contact photolithography (i.e. normal to the mask 22 surface, not at 60° as in Figure 4) with a typical exposure time of 250s (at 0.3 mW/cm^2). The mask 22 contained a bigrating pattern of 0.9μm chrome squares

10 separated by 0.5μm gaps in each direction giving a pitch of 1.4x1.4μm. Development was then carried out in Shipley MF319 for 10 sec followed by a water rinse. Samples were finally baked at 160°C for 45 minutes after first receiving a deep UV exposure to preharden the photoresist (3.36 J/cm^2 at 254nm). This process created a bigrating with two identical modulations each of which had a symmetric profile. The alignment of a

15 nematic on this is therefore expected to consist of two non tilted alignment states (alignment, but no surface tilt) separated by an azimuthal angle of 90°. Such an alignment is not normally of use in display devices, but was prepared for test and comparison purposes.

20 Cells having a cell gap of 0.95μm were then made with these (zero pretilt) bigratings on both inner surfaces arranged so that the groove directions on one surface coincided with the groove directions on the other. These were filled with E7 nematic containing various concentrations of N65 in its isotropic phase. On cooling to room temperature all cells showed two alignment directions as expected. As the states have no surface

25 pretilt, and hence no splay, there is no method (like the flexoelectric coupling in splayed configurations) by which only one state can be selected using applied electrical pulses. However random switching between the states can occur which was seen by pulse-induced domain wall movement.

Rectangular monopolar pulses of various pulse lengths were applied to each cell. Each pulse alternated in sign from the previous pulse to maintain a dc balance. Pulses were separated by a time interval 100 times the pulse length. For each pulse length a voltage existed above which domain wall movement occurred. Figure 3 shows this threshold voltage versus time for two cells; one a cell filled with pure E7, and the other a cell filled with a 2% precured mixture of N65 in E7. The N65 has clearly lowered the voltage threshold to a value of only 5.0 V/μm for a 10.8 ms pulse. In contrast the pure E7 cell shows a much higher voltage switching (15.0 V/μm) and in fact suffered dielectric breakdown for low pulse lengths.

The above results show that the N65 treatment leads to a low voltage bistable switching which is consistent with a low zenithal anchoring energy combined with no in-plane memory anchoring other than the elastic W_ϕ imposed by the bigrating.

In order to obtain fully selective bistable switching one state has to be favoured by the applied pulse. This can be achieved using dc coupling to a flexoelectric polarisation if the two bistable states have the appropriate pretilts. In WO 92/0054, pretilt can be obtained by using obliquely evaporated SiO.

A more controllable method, described in GB2286467-A achieves pretilt by using a bigrating in which both modulations have asymmetric profiles. This method allows a pretilt of typically 17° for one of the bistable states while maintaining a pretilt of 0° for the other state. These surfaces were tested in conjunction with the N65 treatment using the following fabrication process as illustrated in Figure 4.

A thin layer 20 of 1805 photoresist was spun onto ITO coated glass 21 as described above. After softbaking, the layer 20 was exposed through the 1.4x1.4μm pitch mask 22 using an off axis diagonal exposure geometry as shown in figure 4: i.e. exposure at about 60° to the surface normal and about 45° to the mask array of square pixels. The exposure time was set to 540 seconds (at 0.15 mW/cm^2). After development and processing the bigrating was constructed opposite a flat photoresist surface (i.e. no grating and hence zero pretilt) using 10μm cell spacers to allow measurement of the surface pretilt at the bigrating surface.

Table 2 shows the pretilt of the tilted state measured by the crystal rotation method (T. J. Scheffer and J. Nehring, J. Appl. Phys., vol.48, no. 5, p. 1783 (1977)) for cells filled with various mixtures. In all cases the non-tilted state had a pretilt of less than 0.1°.

Mixture used to fill cell	Pretilt (°)
Pure E7	17.5
2% N65 in E7+ pure E7 (1:1)	17.1
2% N65 in E7+ pure E7 (2:1)	15.4
2% N65 in E7	2.2

Table 2.
Surface pretilt modified by the presence of N65.

The pure E7 gave a high pretilt as expected but the addition of 2% N65 (precured) lead to a catastrophic loss of pretilt which means that this treatment is not suitable for a flexoelectric coupled device where a significant pretilt is required in order to achieve dc sensitivity. However further diluting of the 2% mixture via addition of pure E7 allows the pretilt to be at a value close to the pure E7 cell.

Comparison of data in table 1 and table 2 shows that it is possible to obtain a mixture regime which provides weak zenithal anchoring while maintaining surface pretilt. The loss of pretilt for 2% N65 in E7 can be understood by the further weakening of W_θ

5 which allows the nematic to adopt a non tangential orientation with the local surface. This destabilises the high pretilt state with respect to the low pretilt state. Such states are described in GB9502635.7, "liquid crystal device alignment", G. P. Bryan-Brown, C. V. Brown and D. G. McDonnell.

10 The above results have shown one example of how an oligomeric additive (N65) can be mixed with a typical nematic (e.g. E7) to improve the voltage response of a bistable nematic device without compromising other surface parameters such as pretilt.

Example 2

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Another example of a weak anchoring treatment was synthesised using block polymerisation of a thiol and a vinyl ether to form the structure A shown below, the subscript n is number of repeats in a chain.

20
$$-\left[S(CH_2)_6 S\, CH_2CH_2O(CH_2)_6\, O\, CH_2CH_2\right]_n - \quad \ldots A$$
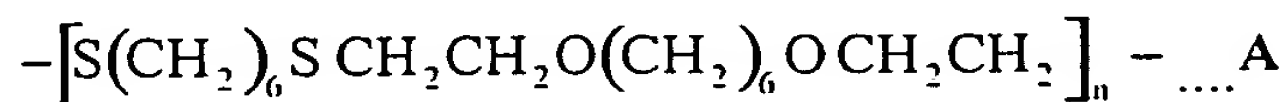
As in example 1, the precursor materials were added to E7 and then cured in a fused silica pre-cell. The cured mixture was then transferred to a second cell whose inner surfaces were coated with hardbaked photoresist. Filling was carried out at 65°C

25 followed by slow cooling to room temperature. One particular cell was filled with a mixture which had been cured from a 5% solution of the precursor materials in E7. This cell showed a schlerien texture with highly mobile domain walls confirming that all in-plane memory anchoring had been lost.

A measurement of the saturation voltage revealed that the zenithal anchoring energy had been lowered to a value of 1.2×10^{-3} N m^{-1}. This is even lower than the values shown in table 1 which indicates that the oligomer units formed in this case are more effective at lowering the surface order parameter of the nematic phase. Once again dilution of the 5% solution into pure E7 revealed a regime on grating surfaces in which weak zenithal anchoring was combined with high (>15°) pretilt.

Therefore the structure **A** is another successful example of an oligomer which can be added to a nematic (e.g. E7) improve the voltage response of a bistable nematic device without compromising other surface parameters such as pretilt.

Example 3

The following structures **B** is a list of example monomers which can also be used to created weak anchoring treatments.

$CH_2 = CH \ O(CH_2)_6O \ CH=CH_2$ HDVE (Hexane -1,6-diol di(vinyl ether)   ...**B**

$CH_2 = CHOC_4H_9$ BVE (Butyl vinyl ether)   ...**B**

$HSCH_2CO_2(CH_2)_2OCOCH \ S_2H$ EGTG (Ethylene glycol bis(thioglycollate)) **B**

$HS(CH_2)_9SH$ NDT (Nonane-1,9-dithiol)   ....**B**

In previous examples low voltage bistable nematic switching has been shown to occur when W_q is lowered. Therefore the materials in **B** have been investigated to determine their effect on W_θ.

Mixtures of these materials were cured before adding to the liquid crystal and the final mixture was tested in cells containing flat hardbaked photoresist on the inner surfaces as described in example 1. Values of W_θ were then obtained using the method described in example 1.

Of the materials listed. EGTG and NDT are monomers with thiol terminations while HDVE and BVE are difunctional and monofunctional `-ene' materials respectively.

5   The first set of mixtures studied are shown in table 3. In each case a percentage of monfunctional BVE has been added to the bifunctional HDVE in order to induce chain termination and so form oligomers with smaller molecular weights. In each case the quoted percentage is the molar quantity of BVE with respect to HDVE. Furthermore the quantity of NDT in each mixture was varied to maintain an equal number of thiol

10   groups and ene groups. To each mixture was added 1% of Igracure 651 (Merck) which acts as a photoinitiator. For each material. curing was carried out under a mercury lamp (2.0 mW/cm^2) for 10 minutes. E7 (Merck) was used as the liquid crystal to which was added 2% of each material (by weight). The results in table 3 shows that the resulting zenithal anchoring energy (W_0) lies in the range $3.6\text{-}8.8\times10^{-3}$ J m^{-2}. Therefore

15   all the mixtures can be considered to be successful in reducing the anchoring from the value found for pure E7 ($>5\times10^{-2}$ J m^{-2}). Furthermore addition of more BVE and hence shorter oligomer chains is found to lead to weaker anchoring.

Material	$W_0 \times10^{-3}$ J m^{-2}
NDT / HDVE / 2% BVE	8.8
NDT / HDVE / 5% BVE	5.9
NDT / HDVE / 20% BVE	3.6

20   Table 3.

Measurement of zenithal anchoring for thiol/diene systems with chain termination.

The correlation of anchoring and molecular length for a given material type was further tested using a set of mixtures containing EGTG, HDVE and BVE. In this case GPC analysis was carried out in order to measure the molecular weights of each material as shown in table 4; Mn is number average of each chain, Mw is average weight per chain, and W_θ is zenithal anchoring energy. The smallest portion of BVE (2%) is indeed found to lead to the longest molecular weights and vice versa. 1% of each of these materials was added to E7 and W_θ was measured. The correlation of W_θ with molecular weight is fairly good considering the errors in the W_θ measurement.

Material	Mn	Mw	$W_\theta \times 10^{-5}$ J m^{-2}
EGTG/ HDVE / 2% BVE	12640	27330	10.9
EGTG / HDVE / 5% BVE	6970	17140	5.3
EGTG/ HDVE / 10% BVE	5000	11550	6.6
EGTG/ HDVE / 20% BVE	2900	6200	4.4

Table 4.

Measurement of zenithal anchoring for thiol/diene systems with chain termination.

To summarise, in this example two sets of materials have been studied both have been found to lead to a reduction in W_θ. Furthermore samples of these materials have also been found to reduce the switching voltages in bistable nematic devices.

CLAIMS

1. A bistable nematic liquid crystal device capable of being switched into two different stable states comprising

5

two cell walls enclosing a layer of nematic liquid crystal material;

electrode structures on both walls;

10 a surface alignment on one or both cell walls providing two alignment directions to liquid crystal molecules with an amount of surface pretilt;

means for distinguishing between switched states of the liquid crystal material;

15 CHARACTERISED BY

means for reducing inelastic azimuthal memory anchoring energy in the surface alignment on one or both cell walls.

20 2. The device of claim 1 and including means for reducing zenithal anchoring energy

3. The device of claim 1 wherein the means for reducing the anchoring energy is an oligomer or short chain polymer which is either spread on the surface or added to the liquid crystal material.

4. The device of claim 3 wherein the oligomer is a material selected from:

Norland N65

$$-\left[S(CH_2)_6 S\, CH_2CH_2O(CH_2)_6 O\, CH_2CH_2\right]_n -$$
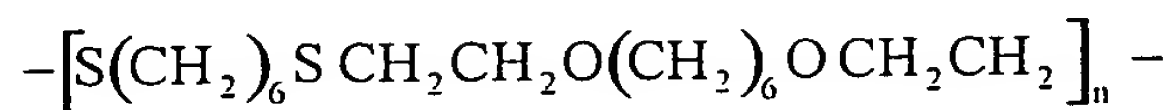
$CH_2 = CH\, O(CH_2)_6O\, CH=CH_2$ HDVE (Hexane -1,6-diol di(vinyl ether)

$CH_2 =CHOC_4H_9$ BVE (Butyl vinyl ether)

$HSCH_2CO_2(CH_2)_2OCOCH\, S_2H$ EGTG (Ethylene glycol bis(thioglycollate))

$HS(CH_2)_9SH$ NDT (Nonane-1,9-dithiol)

5. The device of claim 3 wherein the oligomer is an amount up to 10.% by weight in the liquid crystal material.

6. The device of claim 3 wherein the chain length (n) is less than 100 repeat units.

7. The device of claim 3 wherein the oligomer's parameters of type, concentration, chain length, are arranged to reduce the liquid crystal order parameter at or adjacent the cell wall.

8. The device of claim 3 wherein the ologomer's parameters of type, concentration, chain length, are arranged to change the phase of the liquid crystal material at or adjacent the cell wall.

9. The device of claim 3 wherein the oligomer is a material is a material that has been precured prior to introduction between the cell walls.

10. The device of claim 3 wherein the oligomer is a material that has been precured after introduction between the cell walls.

11. The device of claim 1 wherein the surface alignment is provided by a bigrating surface.

Abstract.

A bistable nematic liquid crystal device comprises a layer of a nematic or long pitch

5   cholesteric material contained between two cells walls. One or both walls are surface

treated to provide two stable alignment directions into which liquid crystal molecules

may switch under the influence of an applied electric field. This surface treatment also

provides pretilt to the molecules and the pretilt angle may be different for the two

alignment directions. The invention improves the switching by removing inelastic

10   azimuthal memory anchoring energy and reducing azimuthal and zenithal anchoring

energy of liquid crystal molecules at the cell walls without substantially changing

molecular pretilt angles. The reduction in anchoring energy may be by a treatment to

the cell walls or by an additive in the liquid crystal material. The treatment and

additive may be an oligomer or short chain polymer applied to the wall prior to

15   assembly in a cell, or as an up to 5% additive. The oligomer may be UV cured

Norland N65 or $-\left[S(CH_2)_6 S\, CH_2CH_2O(CH_2)_6\, O\, CH_2CH_2\right]_n -$ .HDVE (Hexane -

1,6-diol di(vinyl ether, BVE (Butyl vinyl ether, EGTG (Ethylene glycol
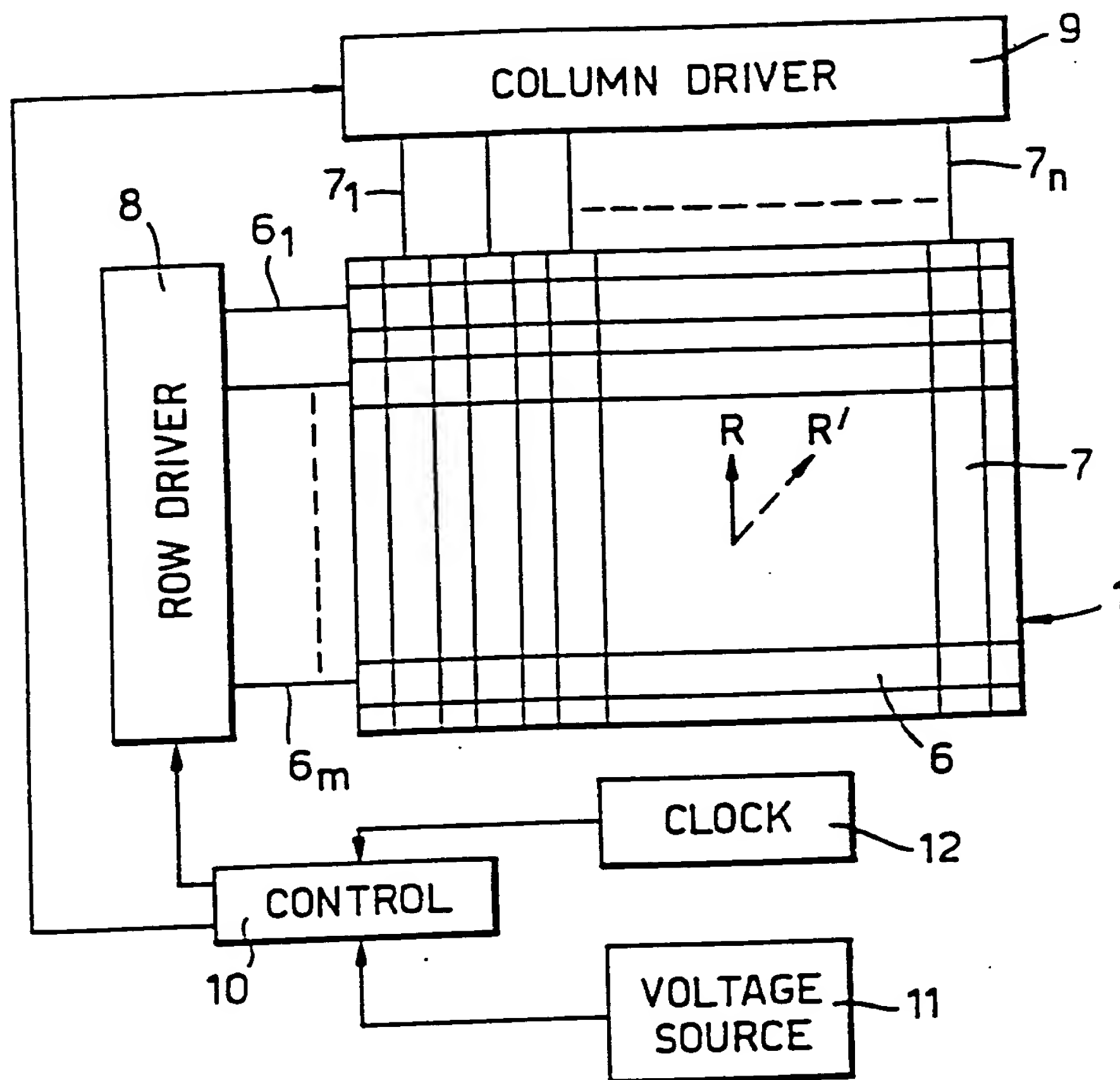
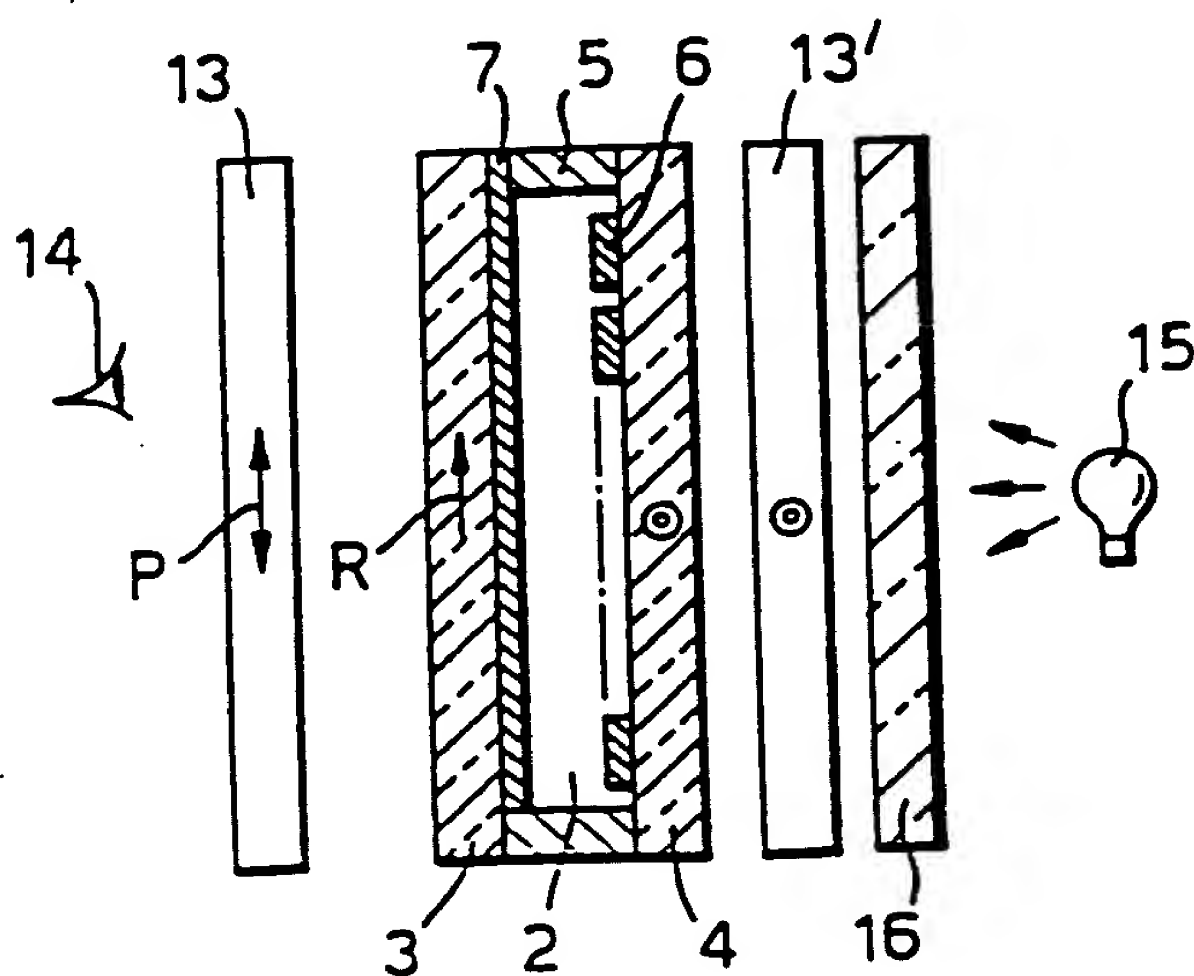bis(thioglycollate)), NDT (Nonane-1,9-dithiol.
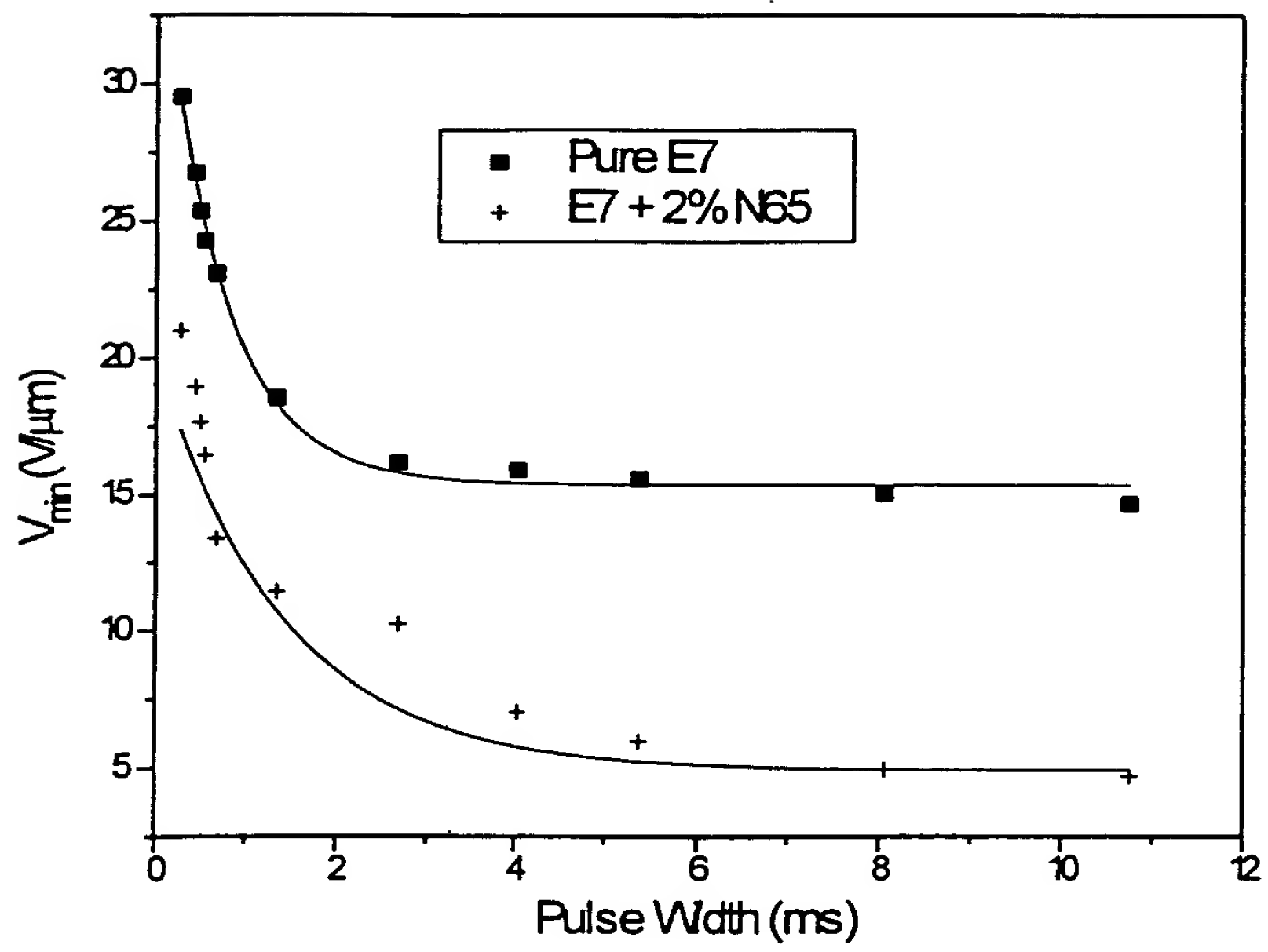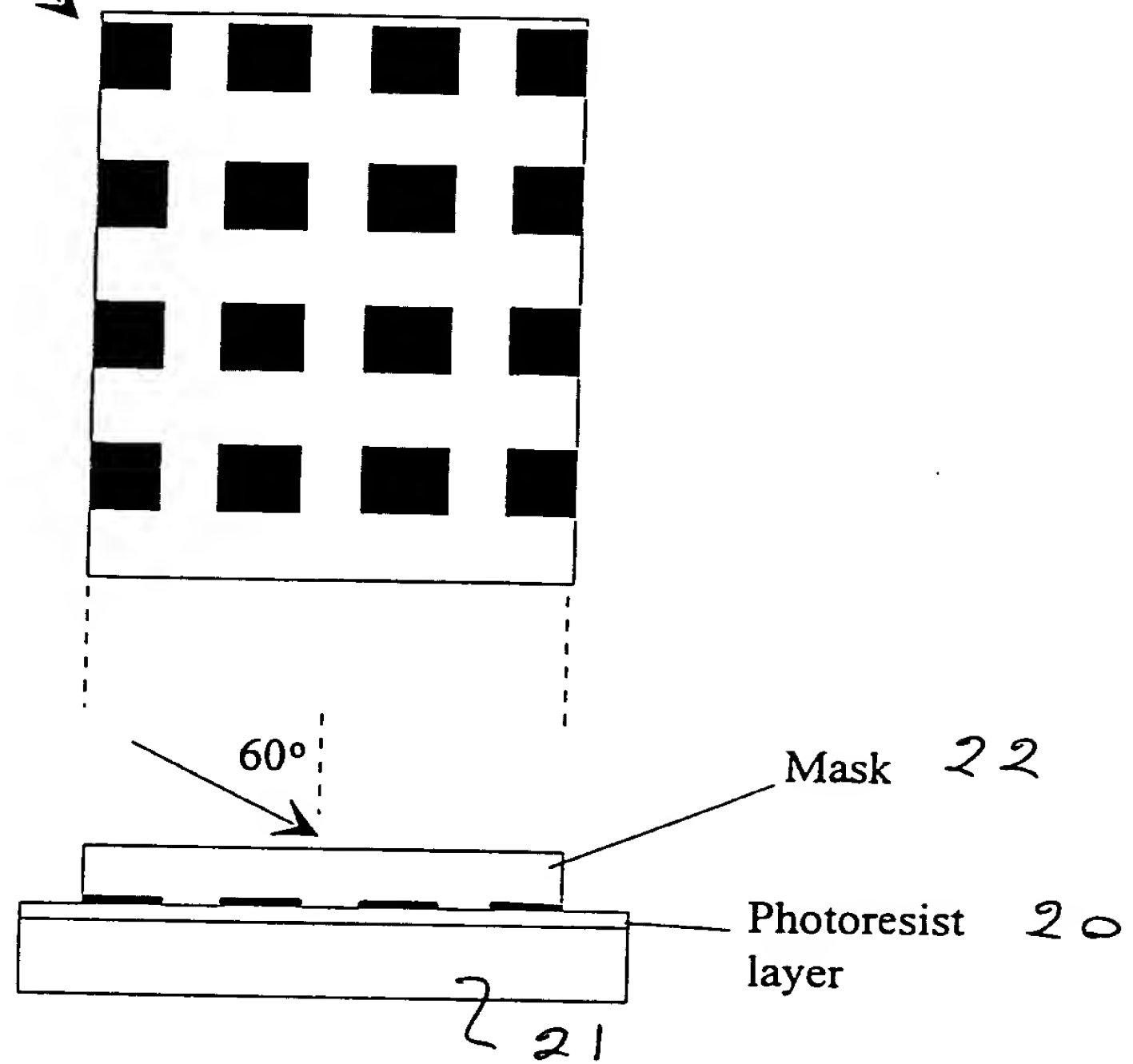
20

Fig.1.

Fig.2.

Figure 3

Figure 3

Figure 4

Exposure
direction

60°

Mask 22

Photoresist 20
layer

21

PCT/GB 98/03011

Hewlett-Packard IP Section, Bristol.

8/10/98